SECURITY CLASSIFICATION OF THIS PAGE

AD-A253 729

DTIC ELECTE AUG 6 1992 S C D

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION Unclassified	
2a SECURITY CLASSIFICATION AUTHORITY	
2b DECLASSIFICATION / DOWNGRADING SCHEDULE	Unlimited
4 PERFORMING ORGANIZATION REPORT NUMBER(S) 14	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION NIST / 6b OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION ONR
6c ADDRESS (City, State, and ZIP Code) A329, Materials Building Gaithersburg, Md 20899	7b ADDRESS (City, State, and ZIP Code) Code 1131 800 N. Quincy Street Arlington, VA 22217-5000
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR / 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-90-F-0011
8c. ADDRESS (City, State, and ZIP Code)	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO / PROJECT NO / TASK NO / WORK UNIT NO

11 TITLE (Include Security Classification)

Moire-Fringe Images of Twin Boundaries in Chemical Vapor Deposited Diamond

12 PERSONAL AUTHOR(S)

D. Shechtman, A. Feldman, M.D. Vaudin, and J.L. Hutchison

13a. TYPE OF REPORT	13b. TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Interim	FROM ____ TO ____	92-07-10	13

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	This document has been approved for public release and sale: its distribution is unlimited

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Features in lattice image micrographs of chemical vapor deposited diamond can be interpreted as Moire fringes that occur when viewing twin boundaries that are inclined to the electron beam. The periodicities in images of inclined twin boundaries with $\Sigma=3$ and $\Sigma=9$ misorientations have been modeled by computer graphic simulation.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE (Include Area Code) / 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Enclosure (1)

OFFICE OF NAVAL RESEARCH

Contract N00014-90-F-0011

R&T Project No. IRMT 025

TECHNICAL REPORT No. 14

MOIRE-FRINGE IMAGES OF TWIN BOUNDARIES IN CHEMICAL VAPOR DEPOSITED DIAMOND

D. Shechtman*, A. Feldman, M.D. Vaudin, and J.L Hutchison**

submitted to

Applied Physics Letters

National Institute of Standards and Technology

Ceramics Division

Gaithersburg, MD 20899

July 10, 1992

*Visiting scientist at the Johns Hopkins University and at NIST from the Technion, Israel.
** University of Oxford, England

MOIRE-FRINGE IMAGES OF TWIN BOUNDARIES IN CHEMICAL VAPOR DEPOSITED DIAMOND[a)]

Dan Shechtman[b)]
Department of Materials Engineering
Technion, Haifa, 32000, Israel

Albert Feldman and Mark D. Vaudin
Ceramics Division
Materials Science and Engineering Laboratory
National Institute of Standards and Technology[c)]
Gaithersburg MD 20899

and

John L. Hutchison
Department of Materials
University of Oxford
Oxford OX1 3PH, England

ABSTRACT

Features in lattice image micrographs of chemical vapor deposited diamond can be interpreted as Moire fringes that occur when viewing twin boundaries that are inclined to the electron beam. The periodicities in images of inclined twin boundaries with $\Sigma=3$ and $\Sigma=9$ misorientations have been modeled by computer graphic simulation.

Key words: chemical vapor deposition, CVD, diamond, twins, lattice images, Moire fringes

[a)]This work was supported in part by the U.S. Office of Naval Research.
[b)]Visiting Professor at the Johns Hopkins University and Guest Scientist at the National Institute of Standards and Technology.
[c)]Technology Administration, U.S. Department of Commerce

MOIRE-FRINGE IMAGES OF TWIN BOUNDARIES IN CHEMICAL VAPOR DEPOSITED DIAMOND

Recent work strongly suggests that lattice defects such as twins and stacking faults play an important role in the growth of diamond films prepared by chemical vapor deposition (CVD)[1]. CVD diamond usually grows as a polycrystalline material consisting of highly twinned grains. Typically, each grain is not a single crystal but consists of many twins, each twin within the grain having a well defined orientation with respect to every other twin within the grain. All of the twins observed in CVD diamond have a common <110> rotation axis.

High resolution transmission electron microscopy (HRTEM) of CVD diamond has revealed a variety of twin boundary types[1-8]. Narayan[3] has noted the presence of twin boundaries classified as $\Sigma=3$ (first order twins) and $\Sigma=9$ (second order twins) in the nomenclature of the coincident site lattice (CSL)[9], where the order n of the twin boundary is such that $\Sigma=3^n$. Twin boundaries have been observed previously in other cubic materials having the diamond lattice structure, such as silicon[10-12] and germanium[13]. In addition to the twin boundaries observed by Narayan, boundaries of types $\Sigma=27$ and $\Sigma=81$ have also been observed in CVD diamond[14] and examples are shown in this letter.

In this letter, we report on several Moire-fringe features observed in high resolution lattice images of CVD diamond. We interpret these features as images of twin boundaries of types $\Sigma=3$ and $\Sigma=9$ where the boundary surface is inclined to the electron beam; the beam passes through both of the twin-related crystals and double diffraction occurs. The periodicities in the resultant image depend on the relative orientations of the twins. By overlapping computer-generated <110> projections of the diamond lattice at the misorientation angles of the crystals, the principal features seen in the these lattice images are reproduced.

We have examined the twinning structure of a fined-grained diamond film grown by microwave-assisted chemical vapor deposition on a single crystal silicon substrate. The film growth parameters were: microwave power - 1 kW; nominal graphite susceptor temperature - 650 °C; gas pressure - 6.6×10^3 Pa; gas flow rate - 260 standard cm^3/min; gas composition - 99.5% H_2, 0.5% CH_4; deposition time - 45 min; growth rate - 0.4 μm/h; total thickness - 0.3 μm; average grain size - ~0.1 μm. The details of the specimen preparation and the HRTEM technique are given in Ref.[1].

We classify the twin boundaries into two categories. The first category consists of planar tilt boundaries lying on crystallographic planes that mirror the bordering twins; these are called 'coherent' boundaries. The second category consists of boundaries that rarely lie on well-defined crystallographic planes and whose orientations may vary from place to place. In this paper, we call these 'noncoherent' boundaries.

Figure 1 shows both coherent and noncoherent twin boundaries in the CVD diamond

specimen. The coherent boundaries are all of type $\Sigma=3$. A noncoherent boundary can be observed meandering across the micrograph. Where the boundary is parallel to the electron beam (V), its image is lighter than the images of coherent boundaries because of preferential ion thinning; this suggests that the noncoherent boundary has greater energy than the coherent boundaries. From the relative orientations of the {111} planes on opposite sides of a boundary, we have identified noncoherent boundaries of types $\Sigma=3$ and $\Sigma=9$. Noncoherent twin boundaries of types $\Sigma=27$ and $\Sigma=81$ can be seen in Fig. 2, which shows a region containing a twin quintuplet (discussed below).

In CVD diamond, $\Sigma=9$, $\Sigma=27$ and $\Sigma=81$ boundaries are usually observed to be noncoherent. This is in marked contrast to observations made in silicon, where $\Sigma=9$ and $\Sigma=27$ boundaries are usually coherent[10,15,16]. Noncoherent boundaries arise when the free surfaces of two twin-related crystals grow toward each other and meet at an arbitrary surface. Because of the relatively low homologous temperature of CVD diamond during the deposition process (650 °C), the atoms in the boundary region have insufficient energy to rearrange once the twins have met; therefore, the boundary plane cannot rotate into a more symmetrical and lower energy orientation. The boundary that is formed results from the detailed kinetics and energetics of the diamond growth specific to a particular specimen. Thus, a noncoherent boundary can even occur when two crystals of the same orientation grow together. There may be some slight displacement of the two crystals relative to each other and there is insufficient energy to allow the boundary to annihilate. Such a displacement is seen in Fig. 1 (W), where two crystals of identical orientation have formed an interface of relatively low density.

Noncoherent boundaries can arise during the early stages of the nucleation and growth of a diamond twin quintuplet, a structure frequently observed to be the origin of growth of a grain[3,7,14]. An example is shown in Fig. 2 where the center of the twin quintuplet is marked ★. Figure 3(a) shows a computer simulation of the twin quintuplet in $\langle 110 \rangle$ projection; in three dimensions, the twin quintuplet consists of five successive tilt boundaries radiating from a common $\langle 110 \rangle$ rotation axis. Four of the boundaries are coherent twin boundaries of type $\Sigma=3$ with a tilt angle of 70.53°. The fifth boundary is of type $\Sigma=81$ with a tilt angle of 77.88°. The difference between the $\Sigma=81$ tilt and the $\Sigma=3$ tilt leaves a small mismatch angle of 7.35° between {111} planes in the twins separated by the $\Sigma=81$ boundary as shown in Fig. 3. The $\Sigma=81$ boundary can be modeled as a $\Sigma=3$ twin boundary containing regularly spaced secondary dislocations to accommodate the mismatch angle[10]. However because of the low homologous temperature referred to above and because this boundary is the last to form during nucleation of a twin quintuplet, the boundary forms in a noncoherent manner inherent to the quintuplet structure.

Several regions in Fig. 1 do not exhibit the typical appearance of $\langle 110 \rangle$ oriented diamond evident throughout most the micrograph. In all cases, these anomalous regions are associated with the noncoherent boundary. The images in these regions can be interpreted as Moire-fringe patterns that result when the twin boundaries are inclined with respect to the electron beam so that the beam passes through two overlapping twins. In Fig. 1, overlapping

twins with boundaries of type $\Sigma=3$ are indicated by X and with boundaries of type $\Sigma=9$ are indicated by Y.

We have modeled the periodicities observed in the images of the inclined $\Sigma=3$ and $\Sigma=9$ noncoherent boundaries using a graphical projection of the diamond lattice viewed along the <110> direction. In the twin quintuplet modeled in Fig. 3(a), each twin is bounded by {111} planes; no attempt has been made to model the $\Sigma=81$ boundary. We have divided the figure into 5 twin domains labeled A, B, C, D and E. Table 1 identifies the boundary type that would occur if one twin, oriented as defined in the twin quintuplet figure, were to border another. If we enlarge the twin in region A to overlap the entire twin quintuplet, we obtain overlap patterns with the periodicities of the CSLs having $\Sigma=3$, $\Sigma=9$, $\Sigma=27$ and $\Sigma=81$ misorientations (Fig. 3(b)). The overlap of region A with region B shows a striped pattern having the same periodicity as the $\Sigma=3$ overlap region labeled X in Fig. 1. The overlap of region A with region C shows a centered hexagonal pattern having the same periodicities as the $\Sigma=9$ overlap region labeled Y in Fig. 1. Furthermore, the relative orientations of the $\Sigma=3$ CSL, the $\Sigma=9$ CSL, and the non-overlapping regions seen in Fig. 3(b) are the same as the relative orientations of the stripes in region X, the hexagonal patterns in region Y and the non-overlapping crystals seen in Fig. 1.

In conclusion, high resolution lattice images of CVD diamond have revealed a highly varied twinning structure. Moire-fringe patterns observed in the micrographs can be interpreted as overlapping twins with boundaries of types $\Sigma=3$ and $\Sigma=9$ that are inclined to the electron beam . A computer graphic simulation has been made to duplicate the periodicities and orientations of these boundary images. The patterns we have identified as being due to overlapping twins show the same periodicities and orientations as the corresponding coincidence site lattices.

REFERENCES

1. D. Shechtman, E.N. Farabaugh, L.H. Robins, A. Feldman and J.L. Hutchison, in Diamond Optics IV, A. Feldman and S. Holly, Editors, SPIE Proc. 1534, 26-43 (1991).

2. B.E. Williams and J.T. Glass, J. Mater. Res. 4, 373 (1989).

3. J. Narayan, J. Mater. Res. 5, 2414 (1990).

4. B.E. Williams, J.T. Glass, R.F. Davis, K. Kobashi and K.L. More, Proc. 1st Int. Symp. Diamond and Diamond Like Films, J.P. Dismukes, editor 202 (1989).

5. G-H.M. Ma, Y.H. Lee and J.T. Glass, J. Mater. Res. 5, 2367 (1990).

6. J. Narayan, A.R. Srivatsa, M. Peters S. Yokota and K.V. Ravi, Appl. Phys. Lett. 53, 1823 (1988).

7. B.E. Williams, H.S. Kong and J.T. Glass, J. Mater. Res. 5, 801 (1990).

8. K. Kobashi, K. Nishimura, K. Miyata, Y. Kawate, J.T. Glass and B.E. Williams, SPIE Diamond Optics, 969, 159 (1988).

9. W. Bollman, Crystal Defects and Crystalline Interfaces (Springer-Verlag, New York, 1970).

10. M.D Vaudin, B. Cunningham and D.G. Ast, Scripta Met. 17, 191 (1983).

11. S. Iijima, Jpn. J. Appl. Phys. 26, 357 (1987).

12. S. Iijima, Jpn. J. Appl. Phys. 26, 365 (1987).

13. Z. Elgat, "Structure of Twin Boundaries in Ge and Spinel", Doctoral Thesis, Cornell University, August 1985.

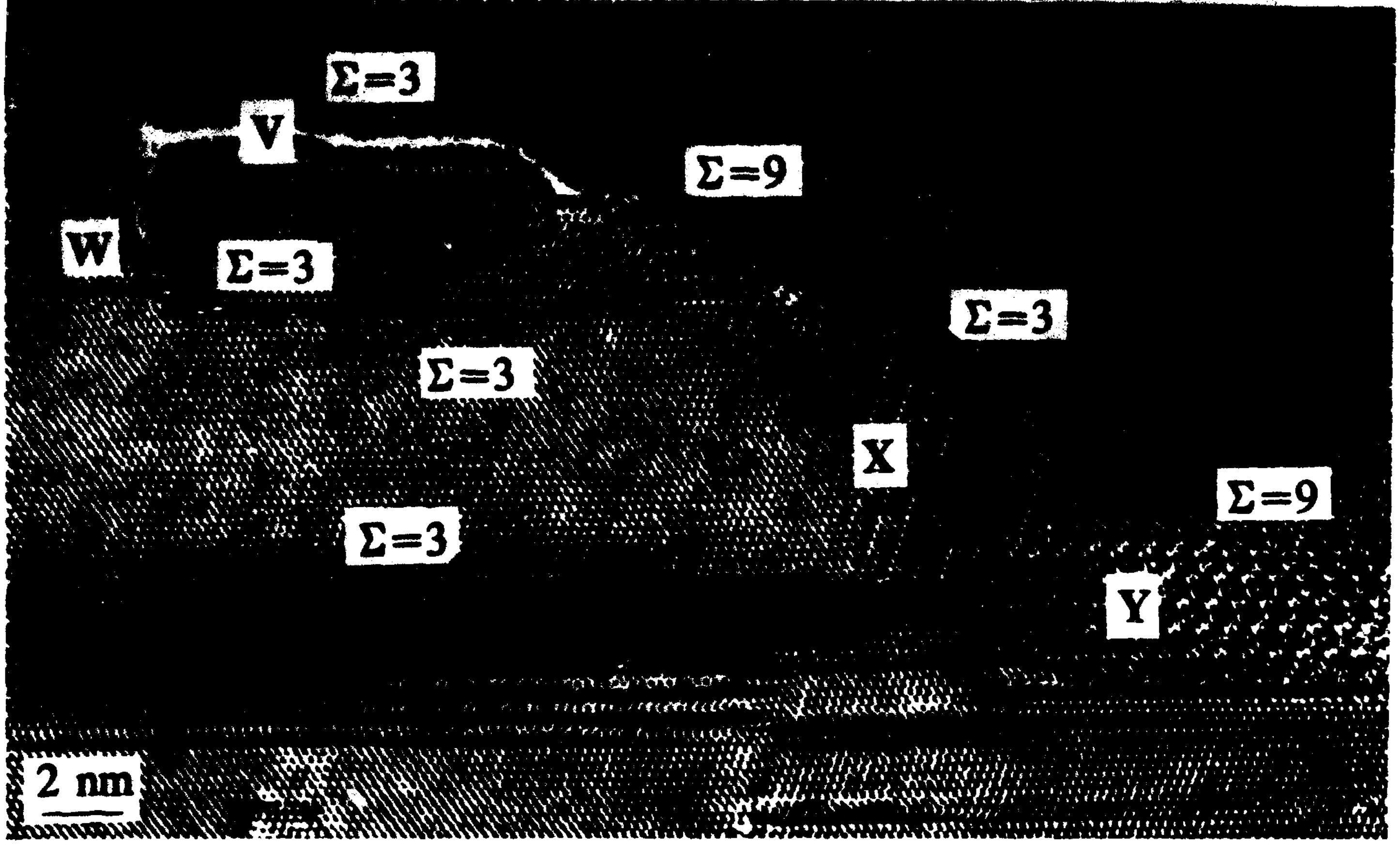
14. D. Shechtman, E.N. Farabaugh, L.H. Robins, A. Feldman and J.L. Hutchison, in preparation.

15. B. Cunningham, H.P. Strunk and D.G. Ast, Scripta Met. 16, 349 (1982).

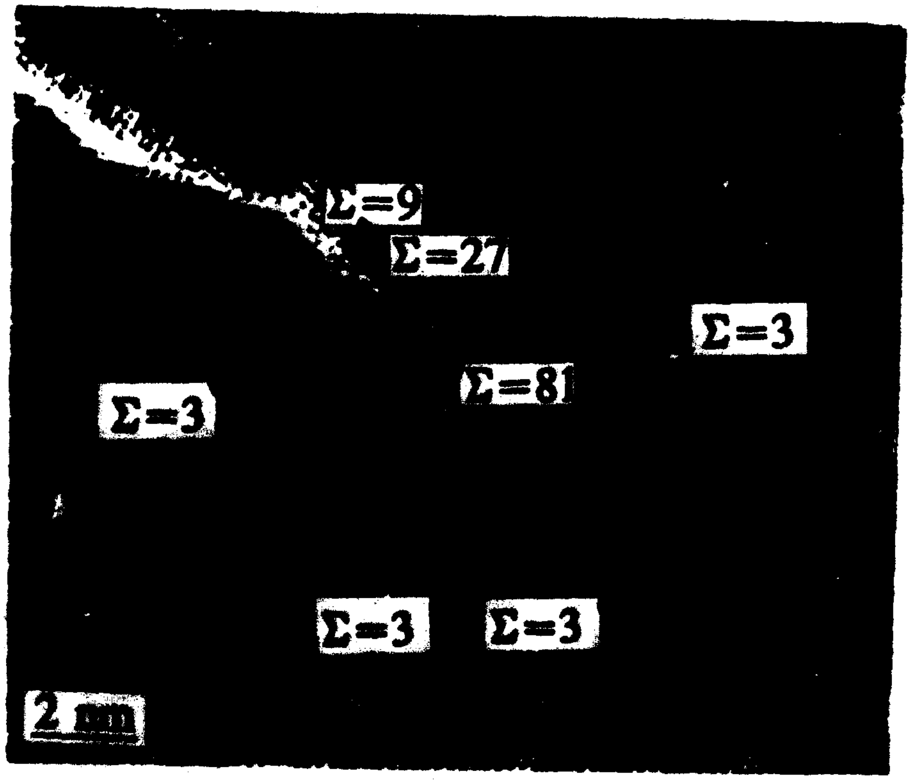
16. B. Cunningham, H.P. Strunk and D.G. Ast, Appl. Phys. Lett. 40(3), (1982).

Table I. Type of twin boundary occurring if one twin in Fig. 3(a), were to border another.

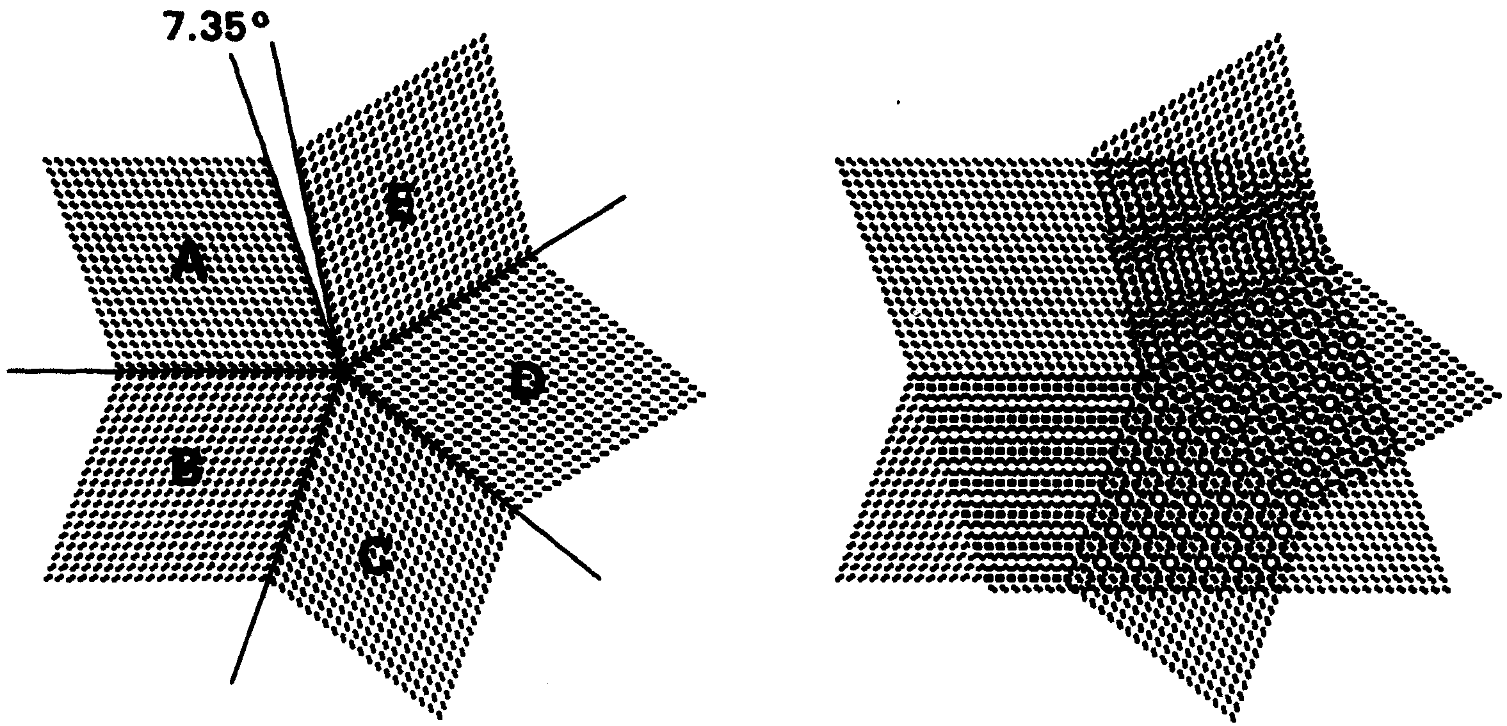
Boundary Type (coincidence site lattice notation)	Adjacent Regions
$\Sigma=3$	A-B, B-C, C-D, D-E
$\Sigma=9$	A-C, B-D, C-E
$\Sigma=27$	A-D, B-E
$\Sigma=81$	A-E



1. Lattice image of a CVD diamond specimen observed in a <110> direction. The figure shows coherent twin boundaries of type Σ=3, noncoherent boundaries of types Σ=3 and Σ=9, and Moire fringes. See text for a discussion of the labeled features.



2. Lattice image of CVD diamond containing a twin quintuplet observed in a <110> direction. Σ=3, Σ=9, Σ=27, and Σ=81 boundaries can be observed.



(a)

(b)

3. (a) Computer model of a twin quintuplet where the {111} planes bounding in each of the twins are indicated by the lines. (b) Overlapping twins having coincidence site lattices of types $\Sigma=3$, $\Sigma=9$, $\Sigma=27$ and $\Sigma=81$. The simulations are observed along a <110> direction.

27 June 1992

Distribution List

Mr. James Arendt
Hughes Aircraft Company
8433 Fallbrook Avenue 270/072
Canoga Park, CA 91304
(838) 702-2890

Mr. Larry Blow
General Dynamics
1525 Wilson Blvd., Suite 1200
Arlington, VA 22209
(703) 284-9107

Mr. Ellis Boudreaux
Code AGA
Air Force Armament Laboratory
Eglin AFB, FL 32542

Dr. Duncan W. Brown
Advanced Technology Materials, Inc.
7 Commerce Drive
Danbury, CT 06810-4131

Dr. Mark A. Cappelli
Stanford University
Mechanical Engineering Department
Stanford, CA 94305
(415) 723-1745

Dr. R. P. H. Chang
Materials Science & Engineering Dept.
2145 Sheridan Road
Evanston, IL 60208
(312) 491-3598

Defense Documentation Center
Cameron Station
Alexandria, VA 22314
(12 copies)

Dr. Bruce Dunn
UCLA
Chemistry Department
Los Angeles, CA 90024
(213) 825-1519

Dr. Al Feldman
Leader, Optical Materials Group
Ceramics Division
Materials Science & Engineering Lab
NIST
Gaithersburg, MD 20899
(301) 975-5740

Dr. John Field
Department of Physics
University of Cambridge
Cavendish Laboratory
Madingley Road
Cambridge CB3 OHE
England
44-223-3377333 Ext. 7318

Dr. William A. Goddard, III
Director, Materials and Molecular
Simulation Center
Beckman Institute
California Institute of Technology
Pasadena, CA 91125
(818) 356-6544 Phone
(818) 568-8824 FAX

Dr. David Goodwin
California Institute of Technology
Mechanical Engineering Dept.
Pasadena, CA 91125
(818) 356-4249

Dr. Kevin Gray
Norton Company
Goddard Road
Northboro, MA 01532
(508) 393-5968

Enclosure (1)

Mr. Gordon Griffith
WRDC/MLPL
Wright-Patterson AFB, OH 45433

Dr. H. Guard
Office of Chief of Naval Research
(ONR Code 1113PO)
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Alan Harker
Rockwell Int'l Science Center
1049 Camino Dos Rios
P.O. Box 1085
Thousand Oaks, CA 91360
(805) 373-4131

Mr. Stephen J. Harris
General Motors Research Laboratories
Physical Chemistry Department
30500 Mound Road
Warren, MI 48090-9055
(313) 986-1305 Phone
(313) 986-8697 FAX
E-mail: SHARRIS@GMR.COM

Mr. Rudolph A. Heinecke
Standard Telecommunication
Laboratories, Ltd.
London Road
Harlow, Essex CM17 9MA
England
44-279-29531 Ext. 2284

Dr. Kelvin Higa
Code 3854
Naval Weapons Center
China Lake, CA 93555-6001

Dr. Curt E. Johnson
Code 3854
Naval Weapons Center
China Lake, CA 93555-6001
(619) 939-1631

Dr. Larry Kabacoff (Code R32)
Officer in Charge
Naval Surface Weapons Center
White Oak Laboratory
10901 New Hampshire
Silver Spring, MD 20903-5000

Mr. M. Kinna
Office of Chief of Naval Research
(ONT Code 225)
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Paul Klocek
Texas Instruments
Manager, Advanced Optical Materials Br.
13531 North Central Expressway
P.O. Box 655012, MS 72
Dallas, TX 75268
(214) 995-6865

Ms. Carol R. Lewis
Jet Propulsion Laboratory
4800 Oak Grove Drive
Mail Stop 303-308
Pasadena, CA 91109
(818) 354-3767

Dr. J.J. Mecholsky, Jr.
University of Florida
Materials Science & Engineering Dept.
256 Rhines Hall
Gainesville, FL 32611
(904) 392-1454

Dr. Russell Messier
202 Materials Research Laboratory
Pennsylvania State University
University Park, PA 16802
(814) 865-2326

Mr. Mark Moran
Code 3817
Naval Weapons Center
China Lake, CA 93555-6001

Mr. Ignacio Perez
Code 6063
Naval Air Development Center
Warminster, PA 18974
(215) 441-1681

Mr. C. Dale Perry
U.S. Army Missile Command
AMSMI-RD-ST-CM
Redstone Arsenal, AL 35898-5247

Mr. Bill Phillips
Crystallume
125 Constitution Drive
Menlo Park, CA 94025
(415) 324-9681

Dr. Rishi Raj
Cornell University
Materials Science & Engineering Dept.
Ithaca, NY 14853
(607) 255-4040

Dr. M. Ross
Office of Chief of Naval Research
(ONR Code 1113)
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Rustum Roy
102A Materials Research Laboratory
Pennsylvania State University
University Park, PA 16802
(814) 863-7040 FAX

Dr. James A. Savage
Royal Signals & Radar Establishment
St. Andrews Road
Great Malvern, Worcs WR14.3PS
England
01-44-684-895043

Mr. David Siegel
Office of Chief of Naval Research
(ONT Code 213)
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Keith Snail
Code 6520
Naval Research Laboratory
Washington, DC 20375
(202) 767-0390

Dr. Y. T. Tzeng
Auburn University
Electrical Engineering Depa tment
Auburn, AL 36849
(205) 884-1869

Dr. Terrell A. Vanderah
Code 3854
Naval Weapons Center
China Lake, CA 93555-6001
(619) 939-1654

Dr. George Walrafen
Howard University
Chemistry Department
525 College Street NW
Washington, DC 20059
(202) 806-6897/6564

Mr. Roger W. Whatmore
Plessey Research Caswell Ltd.
Towcester Northampton NN128EQ
England
(0327) 54760

Dr. Charles Willingham
Raytheon Company
Research Division
131 Spring Street
Lexington, MA 02173
(617) 860-3061

Dr. Robert E. Witkowski
Westinghouse Electric Corporation
1310 Beulah Road
Pittsburgh, PA 15235
(412) 256-1173

Dr. Aaron Wold
Brown University
Chemistry Department
Providence, RI 02912
(401) 863-2857

Dr. Walter A. Yarbrough
260 Materials Research Laboratory
Pennsylvania State University
University Park, PA 16802
(814) 865-2326

Mr. M. Yoder
Office of Chief of Naval Research
(ONR Code 1114SS)
800 North Quincy Street
Arlington, VA 22217-5000

Dr. Robert Pohanka (Code 1131)
Office Of Naval Research
800 N. Quincy Street
Arlington, VA 22217

Dr. David Nelson (Code 1113)
Office Of Naval Research
800 N. Quincy Street
Arlington, VA 22217

Dr. Robert W. Schwartz (Code 38505)
Naval Weapons Center
China Lake, CA 93555